



Europäisches Patentamt
European Patent Office
Office européen des brevets

Publication number:

0 137 963
A1

12

EUROPEAN PATENT APPLICATION

Application number: 84109807.2

Date of filing: 17.08.84

Int. Cl.⁴: C 07 C 49/813, C 07 C 49/84,
C 07 C 62/38, C 07 C 79/36,
C 07 C 147/06, C 07 C 149/273,
C 07 D 317/62, A 01 N 35/06

Priority: 31.07.84 US 634408
07.03.84 US 587331
16.09.83 US 532869

Date of publication of application: 24.04.85
Bulletin 85/17

Designated Contracting States: AT BE CH DE FR GB IT
LI NL SE

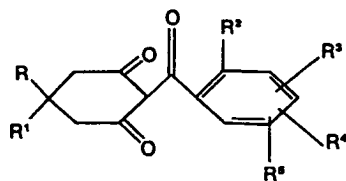
Applicant: STAUFFER CHEMICAL COMPANY, Westport
Connecticut 06881 (US)

Inventor: Michaely, William James, 3161 Birmingham
Drive, Richmond, CA 94806 (US)
Inventor: Kraatz, Gary Wayne, 1423 Bing Drive, San
Jose, CA 95129 (US)

Representative: Kraus, Walter, Dr. et al, Patentanwälte
Kraus, Welsert & Partner Immgardstrasse 15,
D-8000 München 71 (DE)

Certain 2-(2-substituted Benzoyl)-1,3-Cyclohexanediones.

Compounds having the structural formula



wherein R and R' are hydrogen, C₁-C₄ alkyl, R¹OC(O)-, where R¹ is C₁-C₄ alkyl; R² is chlorine, bromine, iodine or C₁-C₄ alkoxy; and R³, R⁴ and R⁵ independently are hydrogen or an aliphatic group.

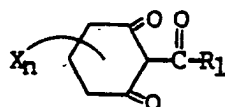
EP 0 137 963 A1

CERTAIN 2-(2-SUBSTITUTED BENZOYL)-1,3-CYCLOHEXANEDIONESCross-Reference to Related Applications

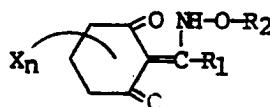
This application is a continuation-in-part application of Serial No. 587,331, filed March 7, 1984; which in turn is a continuation-in-part of application Serial No. 532,869, filed September 16, 1983; which in turn is a continuation-inpart application of 464,251, filed February 9, 1983, now abandoned; which in turn is a continuation-in-part application of Serial No. 361,658, filed March 25, 1982, now abandoned.

Background of the Invention

Compounds having the structural formula



wherein X can be an alkyl, n can be 0, 1, or 2, and R₁ can be phenyl or substituted phenyl are described in Japanese Patent Application 84632-1974 as being intermediates for the preparation of herbicidal compounds of the formula



wherein R₁, X, and n are as defined above and R₂ is alkyl, alkenyl, or alkynyl. Specifically taught herbicidal compounds of this latter group are those where n is 2, X is 5,5-dimethyl, R₂ is allyl and R₁ is phenyl, 4-chlorophenyl or 4-methoxyphenyl.

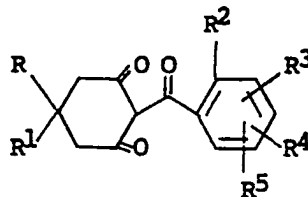
The precursor intermediates for these three specifically taught compounds have no or almost no herbicidal activity.

In contrast, the compounds of this invention have exceptional herbicidal activity. Applicant's compounds must have a chlorine, bromine, iodine or alkoxy substitution in the 2-position of the phenyl moiety of their compounds to obtain the exceptional herbicidal activity. Chlorine is the preferred substituent. The exact reason why such a substitution

imparts exceptional herbicidal activity to the compound is not fully understood.

Description of the Invention

This invention relates to certain novel 2-(2-substituted benzoyl)-cyclohexane-1,3-diones as herbicides. The compounds of this invention have the following structural formula



wherein

R and R¹ are hydrogen, C₁-C₄ alkyl, preferably methyl or isopropyl, R²OC(C)-, where R² is C₁-C₄ alkyl; most preferably R and R¹ are hydrogen;

10 R² is chlorine, bromine, iodine or C₁-C₄ alkoxy, preferably methoxy; most preferably R₂ is chlorine, bromine or methoxy;

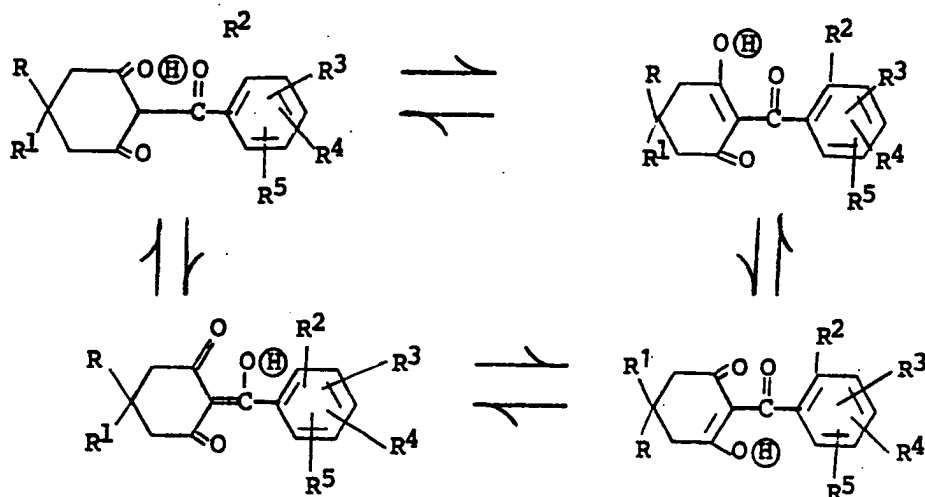
R³, R⁴ and R⁵ independently are hydrogen or an aliphatic group, preferably: (1) hydrogen; (2) halogen, preferably chlorine or bromine; (3) C₁-C₄ alkyl, preferably methyl; (4) C₁-C₄ alkoxy, preferably methoxy; 15 (5) OCF₃; (6) cyano; (7) nitro; (8) C₁-C₄ haloalkyl, more preferably trifluoromethyl; (9) R^bSO_n- wherein R^b is C₁-C₄ alkyl, preferably methyl, C₁-C₄ haloalkyl, phenyl, benzyl, -NR^dR^e wherein R^d and R^e independently are hydrogen or C₁-C₄ alkyl; and n is the integer 0, 1 or 2, preferably 2;



wherein R^c is C₁-C₄ alkyl, (11) R^fC(O) wherein R^f is hydrogen, C₁-C₄ 20 alkyl, C₁-C₄ haloalkyl, C₁-C₄ alkoxy; (12) -NR^gR^h wherein R^g and R^h independently are hydrogen or C₁-C₄ alkyl; or less preferably (13) R³ and R⁴ indetogether can form a ring structure with two adjacent carbon atoms of the phenyl ring.

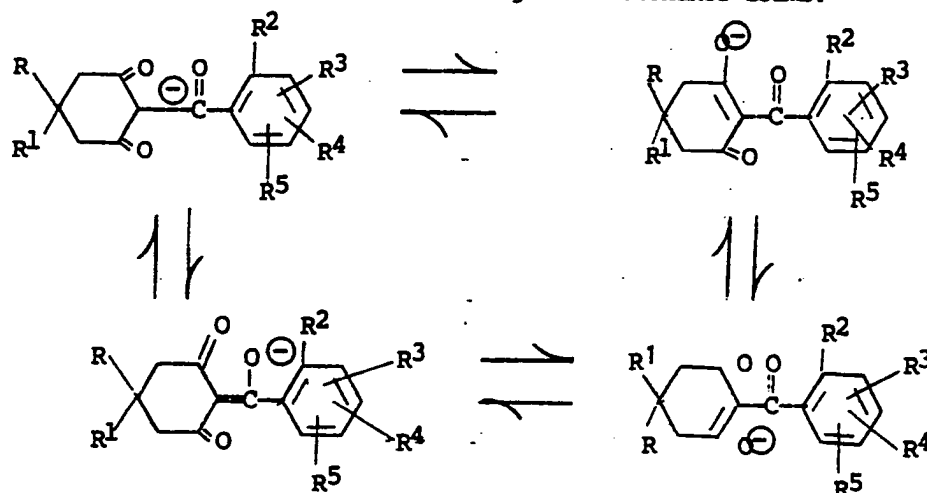
Most preferably, R³ is chlorine, hydrogen, dimethylamino or 25 methoxy. Preferably R⁴ is hydrogen, chlorine, nitro, SO₂CH₃, SO₂N(CH₃)₂ or CF₃. Preferably, R⁵ is hydrogen.

The compounds of this invention can have the following four structural formulae because of tautomerism:



wherein R, R¹, R², R³, R⁴ and R⁵ are as defined above.

The circled proton on each of the four tautomers is reasonably labile. These protons are acidic and can be removed by any base to give a salt having an anion of the following four resonance forms:



wherein R, R¹, R², R³, R⁴ and R⁵ are as defined above.

Examples of cations of these bases are inorganic cations such as alkali metals e.g. lithium, sodium, and potassium alkaline earth metals, e.g. barium, magnesium, calcium and strontium or organic cations such as

substituted ammonium, sulfonium or phosphonium wherein the substituted is an aliphatic or aromatic group.

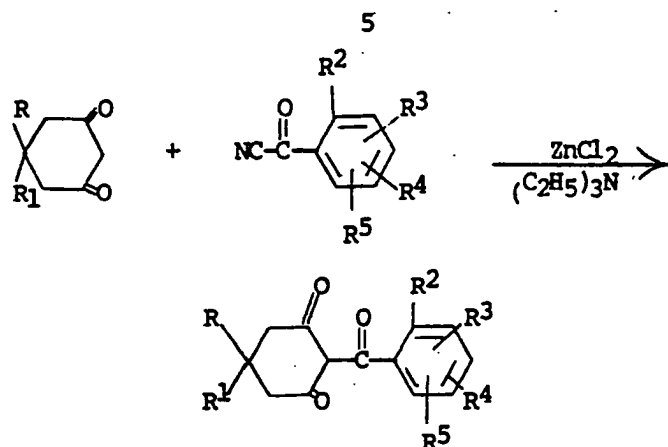
The term "aliphatic group" is used herein in a broad sense to cover a large class of organic groups characterized by being derived from
5 (1) an acyclic (open-chain structure) of the paraffin, olefin and acetylene hydrocarbon series and their derivatives or (2) alicyclic compounds. The aliphatic group can have from 1 to 10 carbon atoms.

The term "aromatic group" is used herein in a broad sense to distinguish from the aliphatic group and includes a group derived from (1)
10 compounds having 6 to 20 carbon atoms and characterized by the presence of at least one benzene ring, including monocyclic, bicyclic and polycyclic hydrocarbons and their derivatives and (2) heterocyclic compounds having 5 to 19 carbon atoms which are similar in structure and are characterized by
15 having an unsaturated ring structure containing at least one atom other than carbon such as nitrogen, sulfur and oxygen and derivatives of these heterocyclic compounds.

In the above description of the compounds of this invention alkyl and alkoxy include both straight and branched configurations; for example, methyl, ethyl, n-propyl, isopropyl, n-butyl, sec-butyl, isobutyl, and
20 tert-butyl.

The compounds of this invention and their salts are active herbicides of a general type. That is, they are herbicidally effective against a wide range of plant species. The method of controlling undesirable vegetation of the present invention comprises applying an herbicidal-
25 ly effective amount of the above-described compounds to the area where control is desired.

The compounds of the present invention can be prepared by the following general method.



Generally, mole amounts of the dione and substituted benzoyl cyanide are used, along with a slight mole excess of zinc chloride. The two reactants and the zinc chloride are combined in a solvent such as methylene chloride. A slight mole excess of triethylamine is slowly added to the reaction mixture with cooling. The mixture is stirred at room temperature for 5 hours.

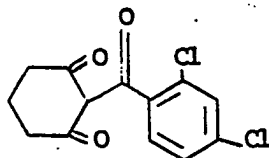
The reaction product is worked up by conventional techniques.

The above-described substituted benzoyl cyanide can be prepared according to the teaching of T.S. Oakwood and C.A. Weisgerber, Organic Synthesis Collected, Vol. III, pp. 122 (1955).

The following example teaches the synthesis of a representative compound of this invention.

EXAMPLE I

2-(2,4-Dichlorobenzoyl)-cyclohexane-1,3-dione

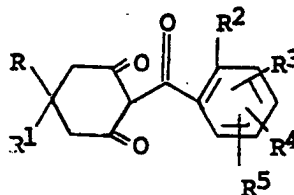


1,3-Cyclohexanedione [11.2 grams (g), 0.1 mole], 20.0 g (0.1 mole) 2,4-dichlorobenzoyl cyanide and 13.6 g (0.11 mole) anhydrous, powdered zinc chloride were combined in 100 milliliters (ml) methylene chloride. Triethylamine (10.1 g, 0.12 mole) was slowly added with cooling.

The reaction mixture was stirred at room temperature for 5 hours and then poured into 2N hydrochloric acid. The aqueous phase was discarded and the organic phase was washed with 150 ml 5% Na_2CO_3 four times. The aqueous washings were combined and acidified with HCl , extracted with methylene chloride, dried and concentrated to yield 25.3 g of crude product. The crude product was dissolved in ether and stirred with 250 ml of 5% copper (II) acetate. The resulting copper salt was filtered, washed with ether and stirred with 6N hydrochloric acid to destroy the salt. The extract was washed with ether to yield 22.15 grams of the desired product m.p. 138-140°C. (77.7% yield). The structure was confirmed by instrumental analysis.

The following is a table of certain selected compounds that are preparable according to the procedure described hereto. Compound numbers are assigned to each compound and are used throughout the remainder of the application.

TABLE I



| Compound Number | R | R ¹ | R ² | R ³ | R ⁴ | R ⁵ | n_D^{30} or m.p. °C |
|-----------------|-----------------|-----------------|----------------|----------------|-------------------|----------------|--------------------------|
| 1 | CH ₃ | CH ₃ | Cl | H | H | H | 1.5613 |
| 2 | CH ₃ | CH ₃ | Cl | H | 4-Cl | H | 1.5655 |
| 3 | CH ₃ | CH ₃ | Cl | H | H | 6-Cl | 103-108 |
| 4* | H | H | Cl | H | 4-Cl | H | 138-140 |
| 5 | CH ₃ | CH ₃ | 2-Br | H | H | H | |
| 6 | CH ₃ | CH ₃ | 2-Cl | H | H | 5-Cl | 74-77 |
| 7 | H | H | Cl | H | H | 5-Cl | 104-107 |
| 8 | H | H | Br | H | H | H | 93-96 |
| 9 | H | H | Cl | H | H | H | 79-87 |
| 10 | H | H | I | H | H | H | 66-70 |
| 11 | H | H | Cl | H | 4-NO ₂ | H | 118-122 |

TABLE I
(continued)

| Compound Number | R | R ¹ | R ² | R ³ | R ⁴ | R ⁵ | N _D ³⁰ or m.p. °C |
|--------------------|--|-----------------|-------------------|---------------------|----------------------------|---------------------|--|
| 12 | H | H | Cl | H | H | 6-Cl | 143-148 |
| 13 | H | H | Cl | H | H | 5-Br | 109-115 |
| 14 | H | H | I | 3-I | H | 5-I | 164-167 |
| 15 | H | H | Cl | H | H | 5-CH ₃ | 60-65 |
| 16 | H | H | Cl | H | 4-CH ₃ O | H | 79-86 |
| 17 | H | H | Cl | H | 4-CH ₃ | H | 60-63 |
| 18 | H | H | Cl | 3-Cl | H | 6-Cl | |
| 19 | H | H | Cl | H | H | 5-CH ₃ O | 77-80 |
| 20 | H | H | Cl | 3-Cl | H | H | 80-90 |
| 21 | H | H | Cl | H | H | 5-CF ₃ | 74-75 |
| 22 | H | H | Cl | H | H | 5-NO ₂ | 140-143 |
| 23 | H | H | Cl | 3-Cl | 4-Cl | H | 152-154 |
| 24 | H | H | Cl | 3-Cl | 4-CH ₃ O | H | 169-170 |
| 25 | H | H | Cl | H | 4-Br | H | 104-107 |
| 26 | CH ₃ | CH ₃ | CH ₃ O | H | H | H | 104-108 |
| 27 | H | H | Cl | H | (a) | H | |
| 28 | H | H | Br | H | H | (b) | |
| 29 | H | H | CH ₃ O | 3-CH ₃ O | H | H | 75-79 |
| 30 | H | H | CH ₃ O | H | H | 5-CH ₃ O | 89-92 |
| 31 | H | H | Br | H | 4-CH ₃ O | 5-CH ₃ O | 92-96 |
| 32 | H | H | Br | H | (4)—OCH ₂ O—(5) | | 63-68 |
| 33 | CH ₃ | CH ₃ | Cl | 3-Cl | 4-Cl | H | 86-89 |
| 34 | H | H | Cl | 3-Cl | H | 5-Cl | |
| 35 | CH ₃ | CH ₃ | Cl | 3-Cl | H | 5-Cl | 105-109 |
| 36 | CH ₃ | CH ₃ | Cl | 3-Cl | 4-Cl | 5-Cl | 137-139 |
| 37 | H | H | Cl | 3-Cl | 4-Cl | 5-Cl | 106-110 |
| 38 | H | H | Cl | H | 4-Cl | 5-Cl | 108-111 |
| 39 | CH(CH ₃) ₂ O-C(=O)- | H | Cl | H | 4-Cl | H | |
| 40 | CH ₃ O-C(=O)- | H | Cl | H | 4-Cl | H | |
| 41 | CH(CH ₃) ₂ | H | Cl | H | 4-Cl | H | |
| 42 | CH(CH ₃) ₂ | H | Cl | 3-Cl | 4-Cl | H | |

TABLE I
(continued)

| Compound Number | R | R ¹ | R ² | R ³ | R ⁴ | R ⁵ | N _D ³⁰ or m.p. °C |
|--------------------|--|-----------------|----------------|-----------------------------------|---|----------------|--|
| 43 | H | H | Cl | H | 4-F | H | |
| 44 | sodium salt of Compound No. 23 | | | | | | 85-94 |
| 45 | isopropylamine salt of Compound No. 23 | | | | | | 160-165 |
| 46 | triethylamine salt of Compound No. 23 | | | | | | 82-85 |
| 47 | potassium salt of Compound No. 23 | | | | | | 107-106 |
| 48 | triethanolammonium salt of Compound No. 39 | | | | | | |
| 49 | sodium salt of Compound No. 43 | | | | | | 60-63 |
| 50 | CH(CH ₃) ₂ | H | Cl | 3-OCH ₃ | 4-Br | H | |
| 51 | H | H | Cl | H | 4-CH ₃ SO ₂ - | H | |
| 52 | H | CH ₃ | Cl | H | 4-Cl | H | |
| 53 | i-C ₄ H ₇ | H | Cl | H | 4-Cl | H | |
| 54 | i-C ₃ H ₅ | H | Cl | 3-OCH ₃ | H | H | |
| 55 | CH ₃ | CH ₃ | Cl | H | 4-CH ₃ SO ₂ - | H | |
| 56 | CH ₃ | CH ₃ | Cl | 3-CH ₃ | 4-Cl | H | |
| 57 | H | H | Cl | 3-CH ₃ | 4-Cl | H | |
| 58 | H | H | Cl | H | 4-C ₂ H ₅ SO ₂ - | H | 98-100 |
| 59 | H | H | Cl | 3-Cl | 4-C ₂ H ₅ SO ₂ - | H | 98-109 |
| 60 | H | H | Cl | H | 4-C ₃ H ₇ SO ₂ - | H | semi-solid |
| 61 | H | H | Cl | 3-OCH ₃ | 4-CH ₃ SO ₂ - | H | 48-59 |
| 62 | CH ₃ | CH ₃ | Cl | H | 4-n-C ₃ H ₇ SO ₂ - | H | semi-solid |
| 63 | H | H | Cl | 3-Cl | 4-n-C ₃ H ₇ SO ₂ - | H | 145-148.5 |
| 64 | H | H | Cl | 3-C ₂ H ₅ S | 4-C ₂ H ₅ SO ₂ - | H | oil |
| 65 | CH ₃ | CH ₃ | Cl | H | 4-C ₂ H ₅ SO ₂ - | H | 103-108 |
| 66 | CH ₃ | CH ₃ | Cl | 3-Cl | 4-C ₂ H ₅ SO ₂ - | H | 108-111 |
| 67 | i-C ₃ H ₇ | H | Cl | H | 4-C ₂ H ₅ SO ₂ - | H | brown gum |
| 68 | H | H | Cl | 3-Cl | 4-CH ₃ SO ₂ - | H | 145-154 |
| 69 | i-C ₃ H ₇ | H | Cl | 3-Cl | 4-CH ₃ SO ₂ - | H | |
| 70 | H | H | Br | H | 4-CH ₃ SO ₂ | H | brown gum |
| 71 | H | H | Cl | H | 4-i-C ₃ H ₇ SO ₂ - | H | |
| 72 | H | H | Cl | H | 4-CH ₃ S- | H | 70-77 |
| 73 | H | H | Cl | 3-Cl | 4-CH ₃ S- | H | |
| 74 | CH ₃ | CH ₃ | Cl | 3-Cl | 4-C ₂ H ₅ SO ₂ - | H | 120-123 |

TABLE I
(continued)

| Compound Number | R | R ¹ | R ² | R ³ | R ⁴ | R ⁵ | N _D ³⁰ or m.p. °C |
|--------------------|-----------------|-----------------|----------------|------------------------------------|---|----------------|--|
| 75 | H | H | Cl | H | 4-n-C ₄ H ₉ SO ₂ - | H | |
| 76 | CH ₃ | CH ₃ | Cl | H | 4-n-C ₄ H ₉ SO ₂ - | H | |
| 77 | H | H | Cl | 3-OC ₂ H ₅ - | 4-CH ₃ SO ₂ - | H | semi-solid |
| 78 | H | H | Cl | 3-OCH ₃ | 4-n-C ₃ H ₇ SO ₂ - | H | golden gum |
| 79 | CH ₃ | CH ₃ | Cl | H | 4-1-C ₃ H ₇ SO ₂ - | H | 125-128 |

* = Prepared in example.



Herbicidal Screening Tests

As previously mentioned, the herein described compounds produced in the above-described manner are phytotoxic compounds which are useful and valuable in controlling various plant species. Selected compounds of this invention were tested as herbicides in the following manner.

- 5 Pre-emergence herbicide test. On the day preceding treatment, seeds of eight different weed species are planted in loamy sand soil in individual rows using one species per row across the width of a flat. The seeds used are green foxtail (FT) (Setaria viridis), watergrass (WG) (Echinochloa crusgalli), wild oat (WO) (Avena fatua), annual morningglory (AMG) (Ipomoea lacunosa), velvetleaf (VL) (Abutilon theophrasti), Indian mustard (MD) (Brassica juncea), redroot pigweed (PW) (Amaranthus retroflexus) or curly dock (CD) (Rumex crispus), and yellow nutsedge (YNG) (Cyperus esculentus). Ample seeds are planted to give about 20 to 40 seedlings per row, after emergence, depending upon the size of the plants.
- 10
- 15 Using an analytical balance, 600 milligrams (mg) of the compound to be tested are weighed out on a piece of glassine weighing paper. The paper and compound are placed in a 60 milliliter (ml) wide-mouth clear bottle and dissolved in 45 ml of acetone or substituted solvent. Eighteen

ml of this solution are transferred to a 60 ml wide-mouth clear bottle and diluted with 22 ml of a water and acetone mixture (19:1) containing enough polyoxyethylene sorbitan monolaurate emulsifier to give a final solution of 0.5% (v/v). The solution is then sprayed on a seeded flat on a linear
 5 spray table calibrated to deliver 80 gallons per acre (748 L/ha). The application rate is 4 lb/acre (4.48 Kg/ha).

After treatment, the flats are placed in the greenhouse at a temperature of 70 to 80°F and watered by sprinkling. Two weeks after treatment, the degree of injury or control is determined by comparison
 10 with untreated check plants of the same age. The injury rating from 0 to 100% is recorded for each species as percent control with 0% representing no injury and 100% representing complete control.

The results of the tests are shown in the following Table II.

| TABLE II | | | | | | | | | |
|-----------------------------------|-----|-----|----|-----|-----|-----|-----|----|-----|
| Pre-Emergence Herbicidal Activity | | | | | | | | | |
| Application Rate — 4.48 kg/ha | | | | | | | | | |
| Compd. No. | FT | WG | WO | AMG | VL | MD | PW | CD | YNG |
| 1 | 100 | 90 | 20 | 40 | 65 | 50 | 35 | | 80 |
| 2 | 80 | 90 | 0 | 30 | 80 | 90 | 20 | | 90 |
| 3 | 0 | 0 | 0 | 40 | 40 | 40 | 0 | | 0 |
| 4 | 100 | 100 | 50 | 35 | 100 | 100 | 90 | | 95 |
| 5 | 100 | 95 | 65 | 35 | 90 | 85 | 50 | | 95 |
| 6 | 50 | 25 | 0 | 25 | 100 | 100 | 35 | | 80 |
| 7 | 80 | 90 | 10 | 60 | 100 | 100 | 100 | | 80 |
| 8 | 95 | 95 | 45 | 40 | 100 | 80 | 95 | | 95 |
| 9 | 95 | 100 | 55 | 30 | 100 | 90 | 100 | | 95 |
| 10 | 100 | 100 | 60 | 20 | 85 | 100 | 100 | | 95 |
| 11 | 85 | 100 | 30 | 40 | 100 | 100 | 100 | | 95 |
| 12 | 85 | 85 | 90 | 75 | 80 | 95 | 90 | | 90 |
| 13 | 85 | 75 | 10 | 10 | 85 | 65 | 95 | | 90 |
| 14 | 40 | 10 | 80 | 0 | 65 | 40 | 65 | | 100 |
| 15 | 40 | 60 | 20 | 30 | 100 | 30 | 75 | | 95 |
| 16 | 80 | 80 | 20 | 55 | 75 | 90 | 40 | | 95 |

TABLE II
(Continued)

| <u>Cmpd.</u> | | | | | | | | | |
|--------------|-----------|-----------|-----------|------------|-----------|-----------|-----------|-----------|------------|
| <u>No.</u> | <u>FT</u> | <u>WG</u> | <u>WO</u> | <u>AMG</u> | <u>VL</u> | <u>MD</u> | <u>PW</u> | <u>CD</u> | <u>YNG</u> |
| 17 | 20 | - | 10 | 25 | 100 | 95 | 85 | | 90 |
| 18 | 65 | - | 30 | 70 | 100 | 100 | 85 | | 90 |
| 19 | 45 | 60 | 0 | 30 | 40 | 0 | 20 | | 60 |
| 20 | 30 | 85 | 20 | 40 | 95 | 85 | 40 | | 45 |
| 21 | 80 | 100 | 0 | 80 | 100 | 100 | 95 | | 95 |
| 22 | 20 | 10 | 0 | 20 | 75 | 30 | 45 | | 10 |
| 23 | 45 | 95 | 10 | 0 | 100 | 85 | 100 | | 95 |
| 24 | - | 100 | 0 | 25 | 70 | 90 | - | | 100 |
| 25 | - | 100 | 25 | 80 | 100 | 100 | - | | 100 |
| 26 | 40 | 15 | 0 | 0 | 0 | 10 | | 0 | 30 |
| 27 | 40 | 80 | 10 | 20 | 60 | 50 | | 30 | 75 |
| 28 | 65 | 75 | 0 | 65 | 100 | 95 | | 75 | 55 |
| 29 | 100 | 95 | 55 | 10 | 80 | 75 | | 85 | 95 |
| 30 | 20 | 20 | 20 | 10 | 40 | 40 | | 50 | 20 |
| 31 | 75 | 95 | 20 | 20 | 100 | 95 | | 75 | 10 |
| 32 | 90 | 85 | 20 | 0 | 100 | 85 | | 75 | 30 |
| 33 | 80 | 70 | 0 | 40 | 20 | 40 | | 90 | 80 |
| 34 | 60 | 40 | 0 | 20 | 95 | 100 | | 100 | 60 |
| 35 | 0 | 10 | 0 | 0 | 10 | 20 | | 20 | 10 |
| 36 | 0 | 0 | 0 | 20 | 100 | 100 | | 100 | 0 |
| 37 | 40 | 0 | 0 | 20 | 100 | 60 | | 90 | - |
| 38 | 10 | 40 | 0 | 20 | 90 | 80 | | 20 | 20 |
| 39 | 80 | 10 | 0 | 0 | 0 | 0 | | 0 | 90 |
| 40 | 60 | 0 | 0 | 0 | 0 | 0 | | 0 | 90 |
| 41 | 100 | 100 | 85 | 40 | 95 | 100 | | 100 | 100 |
| 42 | 60 | 100 | 25 | 0 | 0 | 0 | | 0 | 25 |
| 43 | 100 | 100 | 45 | 40 | 80 | 90 | | 90 | 100 |
| 44 | 90 | 100 | 0 | 60 | 100 | 100 | | 100 | 95 |
| 45 | 100 | 100 | 0 | 60 | 100 | 100 | | 100 | 100 |
| 46 | 20 | 60 | 0 | 100 | 100 | 100 | | 100 | 20 |
| 47 | 60 | 70 | 20 | 100 | 100 | 100 | | 100 | 60 |
| 48 | 60 | 0 | 0 | 0 | 0 | 0 | | 0 | 40 |

TABLE II
(continued)

Compd.

| <u>No.</u> | <u>FT</u> | <u>WG</u> | <u>WO</u> | <u>AMG</u> | <u>VL</u> | <u>MD</u> | <u>PW</u> | <u>CD</u> | <u>YNG</u> |
|------------|-----------|-----------|-----------|------------|-----------|-----------|-----------|-----------|------------|
| 49 | 100 | 100 | 50 | 10 | 60 | 20 | | 90 | 100 |
| 50 | 100 | 100 | 80 | 10 | 60 | 60 | | 90 | 100 |
| 51 | 100 | 100 | 90 | 100 | 100 | 100 | | 85 | 100 |
| 52 | 100 | 100 | 60 | 10 | 100 | 100 | | 60 | 100 |
| 53 | 0 | 20 | 0 | 0 | 20 | 20 | | 0 | 10 |
| 54 | 10 | 45 | 10 | 0 | 0 | 0 | | 0 | 40 |
| 55 | 90 | 100 | 60 | 100 | 100 | 100 | | 90 | 100 |
| 56 | 100 | 100 | 80 | 10 | 60 | 60 | | 90 | 100 |
| 57 | 100 | 100 | 90 | 100 | 100 | 100 | | 85 | 100 |
| 58 | 90 | 95 | 0 | 20 | 20 | 40 | | 40 | 100 |
| 59 | 95 | 100 | 85 | 75 | 100 | 100 | | 90 | 98 |
| 60 | 95 | 100 | 50 | 50 | 100 | 100 | | 90 | 98 |
| 61 | 100 | 100 | 75 | 100 | 100 | 100 | | 95 | 95 |
| 62 | 100 | 100 | 95 | 75 | 100 | 100 | | 100 | 80 |
| 63 | 100 | 100 | 40 | 65 | 100 | 100 | | 100 | 95 |
| 64 | 100 | 100 | 98 | 100 | 100 | 100 | | 100 | 90 |
| 65 | 100 | 100 | 80 | 100 | 100 | 100 | | 100 | 90 |
| 66 | 100 | 100 | 75 | 100 | 100 | 100 | | 100 | 98 |
| 73 | 100 | 100 | 60 | 80 | 100 | 100 | | 75 | 90 |
| 74 | 100 | 100 | 70 | 80 | 100 | 100 | | 80 | 100 |
| 75 | 70 | 100 | 0 | 50 | 100 | 100 | | 100 | 80 |
| 76 | 40 | 90 | 25 | 10 | 100 | 100 | | 100 | 10 |
| 77 | 100 | 100 | 90 | 100 | 100 | 100 | | 85 | - |
| 78 | 100 | 100 | 80 | 100 | 100 | 100 | | 90 | - |

- = Species did not germinate for some reason.
A blank indicates that the weed was not tested.

Post-Emergence Herbicide Test: This test is conducted in an identical manner to the testing procedure for the pre-emergence herbicide test, except the seeds of the eight different weed species are planted 10-12 days before treatment. Also, watering of the treated flats is confined to the soil surface and not to the foliage of the sprouted plants.

The results of the post-emergence herbicide test are reported in Table

III.

TABLE III

Post-Emergence Herbicidal Activity
Application Rate — 4.48 kg/ha

| <u>Cmpd.</u> <u>No.</u> | <u>FT</u> | <u>WG</u> | <u>WO</u> | <u>AMG</u> | <u>VL</u> | <u>MD</u> | <u>PW</u> | <u>CD</u> | <u>YNG</u> |
|----------------------------|-----------|-----------|-----------|------------|-----------|-----------|-----------|-----------|------------|
| 1 | 60 | 70 | 20 | 40 | 60 | 60 | 35 | | 60 |
| 2 | 30 | 70 | 0 | 50 | 90 | 85 | 30 | | 80 |
| 3 | 0 | 30 | 0 | 70 | 100 | 90 | 55 | | 70 |
| 4 | 95 | 98 | 20 | 98 | 100 | 100 | 30 | | 95 |
| 5 | 80 | 80 | 75 | 50 | 60 | 80 | 0 | | 95 |
| 6 | 40 | 40 | 10 | 60 | 100 | 100 | 75 | | 65 |
| 7 | 60 | 75 | 40 | 60 | 100 | 75 | 100 | | 75 |
| 8 | 85 | 80 | 75 | 70 | 95 | 80 | 90 | | 90 |
| 9 | 85 | 80 | 75 | 70 | 95 | 80 | 90 | | 90 |
| 10 | 95 | 85 | 90 | 60 | 95 | 95 | 80 | | 95 |
| 11 | 50 | 80 | 35 | 55 | 100 | 100 | 95 | | 80 |
| 12 | 45 | 75 | 50 | 55 | 75 | 60 | 50 | | 80 |
| 13 | 30 | 60 | 20 | 60 | 80 | 50 | 60 | | 70 |
| 14 | 20 | 10 | 20 | 50 | 45 | 40 | 40 | | 0 |
| 15 | 65 | 95 | 0 | 65 | 95 | 30 | 100 | | 80 |
| 16 | 65 | 80 | 20 | 85 | 85 | 30 | 30 | | 80 |
| 17 | 75 | 80 | 30 | 70 | 100 | 100 | 85 | | 90 |
| 18 | 100 | 95 | 10 | 100 | 100 | 100 | 100 | | 90 |
| 19 | 60 | 80 | 40 | 70 | 100 | 75 | 80 | | 90 |
| 20 | 65 | 80 | 10 | 85 | 95 | 95 | 100 | | 70 |
| 21 | 30 | 55 | 0 | 80 | 100 | 80 | 65 | | 80 |
| 22 | 0 | 30 | 0 | 20 | 45 | 0 | 30 | | 20 |
| 23 | 85 | 90 | 40 | 85 | 100 | 95 | 100 | | 90 |
| 24 | 0 | 80 | 0 | 70 | 90 | 74 | - | | 100 |
| 25 | 100 | 100 | 75 | 90 | 100 | 100 | - | | 100 |
| 26 | 45 | 30 | 0 | 40 | 70 | 65 | | 0 | 45 |
| 27 | 75 | 80 | 30 | 65 | 50 | 45 | | 85 | 85 |
| 28 | 75 | 60 | 60 | 75 | 100 | 70 | | 80 | 25 |
| 29 | 85 | 85 | 85 | 75 | 85 | 65 | | 65 | 85 |

TABLE III

(continued)

| <u>Compd.</u> <u>No.</u> | <u>FT</u> | <u>WG</u> | <u>WO</u> | <u>AMG</u> | <u>VL</u> | <u>MD</u> | <u>PW</u> | <u>CD</u> | <u>YNG</u> |
|-----------------------------|-----------|-----------|-----------|------------|-----------|-----------|-----------|-----------|------------|
| 30 | 75 | 50 | 20 | 10 | 0 | 0 | | 20 | 40 |
| 31 | 60 | 60 | 20 | 40 | 40 | 70 | | 100 | 40 |
| 32 | 60 | 25 | 20 | 40 | 90 | 65 | | 20 | 40 |
| 33 | 10 | 0 | 0 | 10 | 10 | 10 | | 100 | 40 |
| 34 | 10 | 10 | 0 | 5 | 50 | 30 | | 80 | 0 |
| 35 | 0 | 0 | 0 | 10 | 60 | 30 | | 40 | 0 |
| 36 | 0 | 0 | 0 | 20 | 20 | 20 | | 0 | 0 |
| 37 | 0 | 0 | 0 | 30 | 40 | 20 | | 80 | 0 |
| 38 | 10 | 10 | 10 | 20 | 10 | 20 | | 20 | 10 |
| 39 | 40 | 40 | 20 | 0 | 0 | 0 | | 5 | 80 |
| 40 | 90 | 70 | 40 | 20 | 60 | 80 | | 20 | 65 |
| 41 | 60 | 85 | 85 | 20 | 40 | 60 | | 100 | 100 |
| 42 | 60 | 50 | 40 | 70 | 20 | 40 | | 60 | 60 |
| 43 | 100 | 80 | 30 | 60 | 100 | 100 | | 80 | 100 |
| 44 | 80 | 85 | 0 | 60 | 90 | 90 | | 100 | 80 |
| 45 | 90 | 90 | 10 | 100 | 100 | 100 | | 100 | 90 |
| 46 | 80 | 100 | 0 | 60 | 100 | 100 | | 100 | 100 |
| 47 | 100 | 100 | 0 | 60 | 100 | 100 | | 100 | 100 |
| 48 | 40 | 40 | 20 | 10 | 10 | 10 | | 90 | 40 |
| 49 | 40 | 40 | 40 | 80 | 100 | 100 | | 60 | 60 |
| 50 | 80 | 60 | 60 | 50 | 50 | 60 | | 80 | 70 |
| 51 | 80 | 80 | 95 | 100 | 100 | 100 | | 100 | 90 |
| 52 | 60 | 60 | 20 | 20 | 40 | 40 | | 90 | 60 |
| 53 | 10 | 20 | 20 | 0 | 0 | 0 | | 0 | 20 |
| 54 | 20 | 40 | 20 | 5 | 0 | 0 | | 0 | 40 |
| 55 | 40 | 40 | 40 | 60 | 60 | 60 | | 80 | 90 |
| 56 | 80 | 60 | 60 | 50 | 50 | 60 | | 80 | 70 |
| 57 | 80 | 80 | 80 | 95 | 100 | 100 | | 100 | 90 |
| 58 | 60 | 70 | 10 | 70 | 10 | 10 | | 20 | 80 |
| 59 | 100 | 100 | 90 | 100 | - | 100 | | 100 | 50 |
| 60 | 100 | 100 | 100 | 100 | - | 100 | | 100 | 70 |
| 61 | 90 | 85 | 90 | 85 | - | 100 | | 100 | 80 |
| 62 | 100 | 85 | 100 | 75 | 100 | 100 | | 100 | 35 |

TABLE III
(continued)

| <u>Cmpd.</u> <u>No.</u> | <u>FT</u> | <u>WG</u> | <u>WO</u> | <u>AMG</u> | <u>VL</u> | <u>MD</u> | <u>PW</u> | <u>CD</u> | <u>YNG</u> |
|----------------------------|-----------|-----------|-----------|------------|-----------|-----------|-----------|-----------|------------|
| 63 | 70 | 80 | 20 | 100 | 100 | 100 | | 35 | 40 |
| 64 | 75 | 75 | 90 | 70 | 90 | 70 | | 40 | 40 |
| 65 | 100 | 70 | 100 | 55 | 90 | 95 | | 100 | 40 |
| 66 | 100 | 75 | 100 | 90 | 95 | 95 | | 100 | 20 |
| 73 | 100 | 100 | 95 | 100 | 100 | 100 | | 55 | 30 |
| 74 | 100 | 95 | 75 | 100 | 100 | 100 | | 85 | 40 |
| 75 | 100 | 100 | 30 | 95 | 80 | 100 | | 80 | 40 |
| 76 | 80 | 80 | 75 | 75 | 100 | 95 | | 95 | 25 |
| 77 | 80 | 80 | 80 | 90 | 90 | 80 | | 90 | 80 |
| 78 | 80 | 85 | 75 | 85 | 80 | 95 | | 100 | 50 |

Pre-Emergence Multi-Weed Herbicide Test

Several compounds were evaluated at an application rate of 2 lb/acre (2.24 kg/ha) for pre-emergence activity against a larger number of weed speices.

The process was generally similar to the pre-emergence herbicide test described above except that only 300 milligrams of test compound were weighed out and the application rate was 40 gallons per acre.

Redroot pigweed (PW) and curly dock (CD) were eliminated in this test and the following weed species were added:

| | | | |
|-----------------|--------------------|---------------------------|--------|
| <u>Grasses:</u> | downybrone | <u>Bromus tectorum</u> | (DB) |
| | annual ryegrass | <u>Lolium multiflorum</u> | (ARG) |
| | rox-orange sorghum | <u>Sorghum bicolor</u> | (SHC) |
| | hemp sesbania | <u>Sesbania exaltata</u> | (SESB) |
| | nightsaade | <u>Solanum sp.</u> | (SP) |
| | cocklebur | <u>Xattium sp.</u> | (CB) |

The results of the test are shown in Table IV.

TABLE IVPre-Emergence Multi-weed Herbicide Test

| <u>Cmpd.</u> <u>No.</u> | <u>DB</u> | <u>FT</u> | <u>ARG</u> | <u>WG</u> | <u>SEC</u> | <u>WO</u> | <u>BSG</u> | <u>AMG</u> | <u>SESB</u> | <u>VL</u> | <u>SP</u> | <u>MD</u> | <u>YNS</u> | <u>CB</u> |
|----------------------------|-----------|-----------|------------|-----------|------------|-----------|------------|------------|-------------|-----------|-----------|-----------|------------|-----------|
| 67 | 20 | 90 | 25 | 98 | 80 | 60 | 90 | 45 | 90 | 45 | 20 | 85 | 85 | 15 |
| 68 | 65 | 98 | 98 | 100 | 100 | 60 | 95 | 100 | 100 | 100 | 80 | 100 | 95 | 100 |
| 69 | 65 | 100 | 70 | 100 | 100 | 65 | 95 | 100 | 95 | 70 | 65 | 100 | 90 | - |
| 70 | 98 | 100 | 100 | 100 | 100 | 90 | 98 | 90 | 100 | 90 | 60 | 100 | 95 | 80 |
| 71 | 60 | 20 | 100 | 100 | 100 | 80 | 95 | 35 | 40 | 100 | 20 | 90 | 100 | 40 |
| 72 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 90 | 100 | 60 | 100 | 100 | 20 |

The compounds of the present invention are useful as herbicides, especially as pre-emergence herbicides, and can be applied in a variety of ways at various concentrations. In practice, the compounds herein defined are formulated into herbicidal compositions, by admixture, in herbicidally effective amounts, with the adjuvants and carriers normally employed for facilitating the dispersion of active ingredients for agricultural applications, recognizing the fact that the formulation and mode of application of a toxicant may affect the activity of the materials in a given application. Thus, these active herbicidal compounds may be formulated as granules of relatively large particle size, as wettable powders, as emulsifiable concentrates, as powdery dusts, as solutions or as any of several other known types of formulations, depending upon the desired mode of application. Preferred formulations for pre-emergence herbicidal applications are wettable powders, emulsifiable concentrates and granules. These formulations may contain as little as about 0.5% to as much as about 95% or more by weight of active ingredient. A herbicidally effective amount depends upon the nature of the seeds or plants to be controlled and the rate of application varies from about 0.05 to approximately 25 pounds per acre, preferably from about 0.1 to about 10 pounds per acre.

Wettable powders are in the form of finely divided particles which disperse readily in water or other dispersants. The wettable powder is ultimately applied to the soil either as a dry dust or as a dispersion in water or other liquid. Typical carriers for wettable powders include

fuller's earth, kaolin clays, silicas and other readily wet organic or inorganic diluents. Wettable powders normally are prepared to contain about 5% to about 95% of the active ingredient and usually also contain a small amount of wetting, dispersing, or emulsifying agent to facilitate wetting and dispersion.

Emulsifiable concentrates are homogeneous liquid compositions which are dispersible in water or other dispersant, and may consist entirely of the active compound with a liquid or solid emulsifying agent, or may also contain a liquid carrier, such as xylene, heavy aromatic naphthal, isophorone and other non-volatile organic solvents. For herbicidal application, these concentrates are dispersed in water or other liquid carrier and normally applied as a spray to the area to be treated. The percentage by weight of the essential active ingredient may vary according to the manner in which the composition is to be applied, but in general comprises about 0.5% to 95% of active ingredient by weight of the herbicidal composition.

Granular formulations wherein the toxicant is carried on relatively coarse particles, are usually applied without dilution to the area in which suppression of vegetation is desired. Typical carriers for granular formulations include sand, fuller's earth, bentonite clays, vermiculite, perlite and other organic or inorganic materials which absorb or which may be coated with the toxicant. Granular formulations normally are prepared to contain about 5% to about 25% of active ingredients which may include surface-active agents such heavy aromatic naphthas, kerosene or other petroleum fractions, or vegetable oils; and/or stickers such as destrins, glue or synthetic resins.

Typical wetting, dispersing or emulsifying agents used in agricultural formulations include, for example, the alkyl and alkylaryl sulfonates and sulfates and their sodium salts; polyhydric alcohols; and other types of surface-active agents, many of which are available in commerce. The surface-active agent, when used, normally comprises from 0.1% to 15% by weight of the herbicidal composition.

Dusts, which are free-flowing admixtures of the active ingredient with finely divided solids such as talc, clays, flours and other organic and inorganic solids which act as dispersants and carriers for the toxicant, are useful formulations for soil-incorporating application.

- 5 Pastes, which are homogeneous suspensions of a finely divided solid toxicant in a liquid carrier such as water or oil, are employed for specific purposes. These formulations normally contain about 5% to about 95% of active ingredient by weight, and may also contain small amounts of a wetting, dispersing or emulsifying agent to facilitate dispersion. For
10 application, the pastes are normally diluted and applied as a spray to the area to be affected.

- Other useful formulations for herbicidal applications include simple solutions of the active ingredient in a dispersant in which it is completely soluble at the desired concentration, such as acetone, alkyl-
15 ated naphthalenes, xylene and other organic solvents. Pressurized sprays, typically aerosols, wherein the active ingredient is dispersed in finely-divided form as a result of vaporization of a low boiling dispersant solvent carrier, such as the Freons, may also be used.

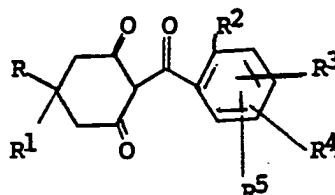
- The phytotoxic compositions of this invention are applied to the
20 plants in the conventional manner. Thus, the dust and liquid compositions can be applied to the plant by the use of power-dusters, boom and hand sprayers and spray dusters. The compositions can also be applied from airplanes as a dust or a spray because they are effective in very low dosages. In order to modify or control growth of germinating seeds or
25 emerging seedlings, as a typical example, the dust and liquid compositions are applied to the soil according to conventional methods and are distributed in the soil to a depth of at least 1/2 inch below the soil surface. It is not necessary that the phytotoxic compositions be admixed with the soil particles since these compositions can also be applied merely by
30 spraying or sprinkling the surface of the soil. The phytotoxic compositions of this invention can also be applied by addition to irrigation water supplied to the field to be treated. This method of application permits the penetration of the compositions into the soil as the water is absorbed therein. Dust compositions, granular compositions or liquid

formulations applied to the surface of the soil can be distributed below the surface of the soil by conventional means such as discing, dragging or mixing operations.

The phytotoxic compositions of this invention can also contain
 5 other additaments, for example, fertilizers and other herbicides, pesticides and the like, used as adjuvant or in combination with any of the above-described adjuvants. Other phytotoxic compounds useful in combination with the above-described compounds include, for example, anilides such as 2-benzothiazole-2-yloxy-N-methyl acetanilide, 2-chloro-2',6'-di-
 10 methyl-N-(n-propylethyl) acetanilide, 2-chloro-2',6'-diethyl-N-(butoxy-methyl) acetanilide; 2,4-dichlorophenoxyacetic acids, 2,4,5-trichlorophenoxyacetic acid, 2-methyl-4-chlorophenoxyacetic acid and the salts, esters and amides thereof; triazine derivatives, such as 2,4-bis(3-methoxypropyl-amino)-6-methylthio-s-triazine, 2-chloro-4-ethylamino-6-isopropylamino-s-
 15 triazine, and 2-ethylamino-4-isopropyl-amino-6-methyl-mercapto-s-triazine; urea derivatives, such as 3-(3,5-dichlorophenyl)-1,1-dimethylurea and 3-(p-chlorophenyl)-1,1-dimethylurea; and acetanides such as N,N-diallyl- α -chloroacetamide, and the like; benzoic acids such as 3-amino-2,5-dichlorobenzoic acid; thiocarbamates such as S-(1,1-dimethylbenzyl)-piperi-
 20 dene-1-carbothioate, 3-(4-chlorophenyl)-methyl diethylcarbothioate, ethyl-1-hexahydro-1,4-azepine-1-carbothioate, S-ethyl-hexahydro-1H-azepine-1-carbothioate, S-propyl N,N-dipropylthiocarbamate, S-ethyl N,N-dipropylthiocarbamate, S-ethyl cyclohexylethylthiocarbamate, S-ethyl hexahydro-1H-azepine-1-carbothioate and the like; anilines such as 4-(methylsulfonyl)-
 25 2,6-dinitro-N,N-substituted aniline, 4-trifluoromethyl-2,6-dinitro-N,N-din-propyl aniline, 4-trifluoromethyl-2,6-dinitro-N-ethyl-N-butyl aniline, 2-[4-(2,4-dichlorophenoxy)phenoxy]propanoic acid, 2-[1-(ethoxyimino)-butyl]-5-[2-ethylthio]propyl]-3-hydroxy-2-cyclohexene-1-one, (+)-butyl-2-[4-[(5-trifluoromethyl)-2-pyridinyl]oxy]phenoxy]propanate, sodium
 30 5-[2-chloro-4-(trifluoromethyl)phenoxy]-2-nitrobenzoate, 3-isopropyl-1H-2,1,3-benzothiadiazine-4(3H)-one-2,2-dioxide, and 4-amino-6-tert-butyl-3-(methylthio)-s-triazin-5(4H)-one or (4-amino-6-(1,1-dimethylethyl)-3-(methylthio)-1,2,4-triazin-5(4H)-one) and S-(O,O-diisopropyl)-benzene sul-
 fonamide. Fertilizers useful in combination with the active ingredients
 35 include, for example, ammonium nitrate, urea and superphosphate. Other useful additaments include materials in which plant organisms take root and grow such as compost, manure, humus, sand, and the like.

WE CLAIM:

1. A compound having the structural formula

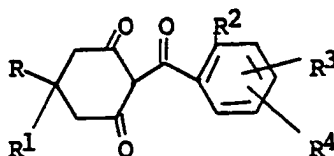


wherein

R and R¹ are hydrogen, C₁-C₄ alkyl, R^aOC(O)-, where R^a is C₁-C₄ alkyl;

5 R² is chlorine, bromine, iodine or C₁-C₄ alkoxy; and

R³, R⁴ and R⁵ independently are hydrogen or an aliphatic group, and their salts with the proviso that compounds having the structural formula



wherein

10 R and R¹ are hydrogen or C₁-C₄ alkyl;

R² is chlorine, bromine, or iodine;

R³ is hydrogen, iodine or chlorine; and

R⁴ is hydrogen, halogen, C₁-C₄ alkyl, C₁-C₄ alkoxy, nitro, or trifluoromethyl are excluded.

2. The compounds of Claim 1 wherein R and R¹ are hydrogen or C₁-C₄ alkyl; R² is chlorine, bromine, iodine or C₁-C₄ alkoxy; R³, R⁴ and R⁵ independently are hydrogen, halogen, C₁-C₄ alkyl, C₁-C₄ alkoxy, OCF₃, cyano, nitro, C₁-C₄ haloalkyl, R^bSO_n wherein R^b is C₁-C₄ alkyl; C₁-C₄ haloalkyl, phenyl, benzyl, -NR^dR^e wherein R^d and R^e independently are hydrogen and C₁-C₄ alkyl; and n is the integer 0, 1 or 2; R^cC(O)NH- wherein R^c is C₁-C₄ alkyl; 15 R^fC(O)- wherein R^f is hydrogen, C₁-C₄ alkyl, C₁-C₄ haloalkyl, C₁-C₄ alkoxy; 20 or -NR^gR^h wherein R^g and R^h independently are hydrogen or C₁-C₄ alkyl and their salts.

3. The compounds of Claim 1 wherein R and R¹ are hydrogen or methyl; R² is chlorine or methoxy; R³ is hydrogen, chlorine, dimethylamino or

methoxy; R^4 is hydrogen, chlorine, nitro, SO_2CH_3 , $SO_2N(CH_3)_2$ or CF_3 ; and R^5 is hydrogen and their salts.

4. The compounds of Claim 3 wherein R^3 is substituted at the 3-position, R^4 is substituted at the 4-position and R^5 is substituted at the 5- or 6-position and their salts.

5. The compounds of Claim 3 wherein R and R^1 are hydrogen; R^2 is chlorine or methoxy; R^3 is hydrogen, 3-chlorine, 4-methoxy or 3-dimethylamino and R^4 is 4-chlorine, 4- CH_3SO_2 - or 4- CF_3SO_2 ; and R^5 is hydrogen and their salts.

6. The compounds of Claim 2 wherein R^2 is chlorine and their salts.

7. The compound of Claim 1 wherein R is methyl, R^1 is methyl, R^2 is chlorine, R^3 is hydrogen, R^4 is hydrogen, and R^5 is 6-chlorine and its salts.

8. The compound of Claim 1 wherein R is hydrogen, R^1 is hydrogen, R^2 is chlorine, R^3 is hydrogen, R^4 is hydrogen, R^5 is 6-chlorine and its salts.

9. The compound of Claim 1 wherein R is hydrogen, R^1 is hydrogen, R^2 is chlorine, R^3 is hydrogen, R^4 is 4-chlorine and R^5 is hydrogen and its salts.

10. The compound of Claim 1 wherein R is hydrogen, R^1 is hydrogen, R^2 is chlorine, R^3 is 3-chlorine and R^4 is hydrogen and R^5 is 6-chlorine and its salts.

11. The compound of Claim 1 wherein R is hydrogen, R^1 is hydrogen, R^2 is chlorine, R^3 is hydrogen, R^4 is hydrogen and R^5 is 5-trifluoromethyl and its salts.

12. The compound of Claim 1 wherein R is hydrogen, R^1 is hydrogen, R^2 is chlorine, R^3 is 3-chlorine, R^4 is 4-chlorine and R^5 is hydrogen and its salts.

13. The compound of Claim 1 wherein R is hydrogen, R¹ is hydrogen, R² is chlorine, R³ is 3-chlorine, R⁴ is 4-methoxy and R⁵ is hydrogen and its salts.

14. The compound of Claim 1 wherein R is hydrogen, R¹ is hydrogen, R² is chlorine, R³ is hydrogen, R⁴ is 4-bromine and R⁵ is hydrogen and its salts.

15. The compound of Claim 1 wherein R is hydrogen, R¹ is hydrogen, R² is methoxy, R³ is 3-methoxy, R⁴ is hydrogen and R⁵ is hydrogen and its salts.

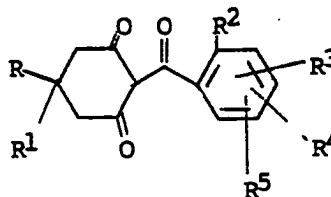
16. The compound of Claim 1 wherein R is isopropyl, R¹ is hydrogen, R² is chlorine, R³ is hydrogen, R⁴ is 4-chlorine and R⁵ is hydrogen and its salts.

17. The compound of Claim 1 wherein R is isopropyl, R¹ is hydrogen, R² is chlorine, R³ is 3-CH₃, R⁴ is 4-CH₃SO₂ and R⁵ is hydrogen and its salts.

18. The compound of Claim 1 wherein R is hydrogen, R¹ is hydrogen, R² is chlorine, R³ is hydrogen, R⁴ is 4-CH₃SO₂ and R⁵ is hydrogen and its salts.

19. The sodium, isopropylamine, triethylamine and potassium salts of the compound of Claim 12.

20. The method of controlling undesirable vegetation comprising applying to the area where control is desired, an herbicidally effective amount of a compound having the formula

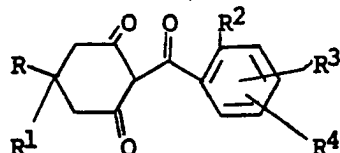


wherein

R and R¹ are hydrogen, C₁-C₄ alkyl, R²OC(O)-, where R² is C₁-C₄ alkyl;

R² is chlorine, bromine, iodine or C₁-C₄ alkoxy; and

R³, R⁴ and R⁵ independently are hydrogen or an aliphatic group with
5 the proviso that compounds having the structural formula



wherein

R and R¹ are hydrogen or C₁-C₄ alkyl;

R² is chlorine, bromine, or iodine;

R³ is hydrogen, iodine or chlorine; and

10 R⁴ is hydrogen, halogen, C₁-C₄ alkyl, C₁-C₄ alkoxy, nitro, or trifluoromethyl are excluded.

21. The method of Claim 20 wherein R and R¹ are hydrogen or C₁-C₄ alkyl; R² is chlorine, bromine, iodine or C₁-C₄ alkoxy; R³, R⁴ and R⁵ independently are hydrogen, halogen, C₁-C₄ alkyl, C₁-C₄ alkoxy, OCF₃,
15 cyano, nitro, C₁-C₄ haloalkyl, R^bSO_n wherein R^b is C₁-C₄ alkyl; C₁-C₄ haloalkyl, phenyl, benzyl, -NR^dR^e wherein R^d and R^e independently are hydrogen and C₁-C₄ alkyl; and n is the integer 0, 1 or 2; R^cC(O)NH- wherein R^c is C₁-C₄ alkyl; R^fC(O)- wherein R^f is hydrogen, C₁-C₄ alkyl, C₂-C₄ haloalkyl, C₁-C₄ alkoxy; or -NR^gR^h wherein R^g and R^h independently are hydrogen or
20 C₁-C₄ alkyl and their salts.

22. The method of Claim 20 wherein R and R¹ are hydrogen or methyl; R² is chlorine or methoxy; R³ is hydrogen, chlorine or methoxy; R⁴ is hydrogen, chlorine, nitro, SO₂CH₃, SO₂N(CH₃)₂ or CF₃; and R⁵ is hydrogen and their salts.

23. The method of Claim 22 wherein R³ is substituted at the 3-position, R⁴ is substituted at the 4-position and R⁵ is substituted at the 5- or 6-position and their salts.

24. The method of Claim 22 wherein R and R¹ are hydrogen; R² is chlorine or methoxy; R³ is hydrogen, 3-chlorine, 3-methoxy or

24

3-dimethylamino; R^4 is 4-chlorine, 4- CH_2SO_2 , or 4- CF_3SO_2 ; and R^5 is hydrogen and their salts.

25. The method of Claim 24 wherein R^2 is chlorine and their salts.

5 26. The method of Claim 20 wherein R is methyl, R^1 is methyl, R^2 is chlorine, R^3 is hydrogen, R^4 is hydrogen, and R^5 is 6-chlorine and its salts.

27. The method of Claim 20 wherein R is hydrogen, R^1 is hydrogen, R^2 is chlorine, R^3 is hydrogen, R^4 is hydrogen, R^5 is 6-chlorine
10 and its salts.

28. The method of Claim 20 wherein R is hydrogen, R^1 is hydrogen, R^2 is chlorine, R^3 is hydrogen, R^4 is 4-chlorine and R^5 is hydrogen and its salts.

29. The method of Claim 20 wherein R is hydrogen, R^1 is hydrogen, R^2 is chlorine, R^3 is 3-chlorine and R^4 is hydrogen and R^5 is
15 6-chlorine and its salts.

30. The method of Claim 20 wherein R is hydrogen, R^1 is hydrogen, R^2 is chlorine, R^3 is hydrogen, R^4 is hydrogen and R^5 is 5-trifluoromethyl and its salts.

20 31. The method of Claim 20 wherein R is hydrogen, R^1 is hydrogen, R^2 is chlorine, R^3 is 3-chlorine, R^4 is 4-chlorine and R^5 is hydrogen and its salts.

32. The method of Claim 20 wherein R is hydrogen, R^1 is hydrogen, R^2 is chlorine, R^3 is 3-chlorine, R^4 is 4-methoxy and R^5 is hydrogen
25 and its salts.

33. The method of Claim 20 wherein R is hydrogen, R^1 is hydrogen, R^2 is chlorine, R^3 is hydrogen, R^4 is 4-bromine and R^5 is hydrogen and its salts.

34. The method of Claim 20 wherein R is hydrogen, R¹ is hydrogen, R² is methoxy, R³ is 3-methoxy, R⁴ is hydrogen and R⁵ is hydrogen and its salts.

35. The method of Claim 20 wherein R is isopropyl, R¹ is hydrogen, R² is chlorine, R³ is hydrogen, R⁴ is 4-chlorine and R⁵ is hydrogen and its salts.

36. The method of Claim 20 wherein R is hydrogen, R¹ is hydrogen, R² is chlorine, R³ is 3-CH₃O, R⁴ is 4-CH₃SO₂ chlorine and R⁵ is hydrogen and its salts.

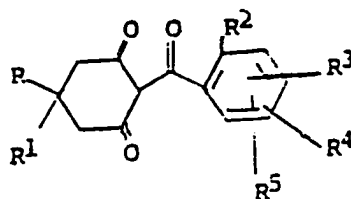
10 37. The method of Claim 20 wherein R is hydrogen, R¹ is hydrogen, R² is chlorine, R³ is hydrogen, R⁴ is 4-CH₃SO₂ and R⁵ is hydrogen and its salts.

38. The sodium, isopropylamine, triethylamine and potassium salts of the method of Claim 31.

- 26 -

Claims for Austria

1. Process for preparing compounds having the structural formula



wherein

R and R¹ are hydrogen, C₁-C₄ alkyl, R²OC(O)-, where R² is C₁-C₄ alkyl;

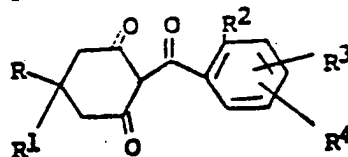
alkyl;

5

R² is chlorine, bromine, iodine or C₁-C₄ alkoxy; and

R³, R⁴ and R⁵ independently are hydrogen or an aliphatic group,

and their salts with the proviso that compounds having the structural formula



wherein

R and R¹ are hydrogen or C₁-C₄ alkyl;

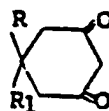
R² is chlorine, bromine, or iodine;

R³ is hydrogen, iodine or chlorine; and

R⁴ is hydrogen, halogen, C₁-C₄ alkyl, C₁-C₄ alkoxy, nitro, or trifluoromethyl are excluded.

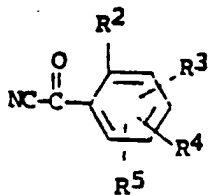
10

comprising reacting a substituted dione of the general formula II



with a substituted benzoyl cyanide of the general formula III

5



and working up the reaction product by conventional techniques.

- 27 -

2. The process of Claim 1 wherein R and R¹ are hydrogen or C₁-C₄
 15 alkyl; R² is chlorine, bromine, iodine or C₁-C₄ alkoxy; R³, R⁴ and R⁵ inde-
 pendently are hydrogen, halogen, C₁-C₄ alkyl, C₁-C₄ alkoxy, OCF₃, cyano,
 nitro, C₁-C₄ haloalkyl, R^bSO_n wherein R^b is C₁-C₄ alkyl; C₁-C₄ haloalkyl,
 phenyl, benzyl, -NR^dR^e wherein R^d and R^e independently are hydrogen and C₁-C₄
 alkyl; and n is the integer 0, 1 or 2; R^cC(O)NH- wherein R^c is C₁-C₄ alkyl;
 20 R^fC(O)- wherein R^f is hydrogen, C₁-C₄ alkyl, C₁-C₄ haloalkyl, C₁-C₄ alkoxy;
 or -NR^gR^h wherein R^g and R^h independently are hydrogen or C₁-C₄ alkyl and
 their salts.

3. The process of Claim 1 wherein R and R¹ are hydrogen or
 methyl; R² is chlorine or methoxy; R³ is hydrogen, chlorine, dimethylamino or
 methoxy; R⁴ is hydrogen, chlorine, nitro, SO₂CH₃, SO₂N(CH₃)₂ or CF₃; and R⁵
 is hydrogen and their salts.

4. The process of Claim 3 wherein R³ is substituted at the
 3-position, R⁴ is substituted at the 4-position and R⁵ is substituted at
 5 the 5- or 6-position and their salts.

5. The process of Claim 3 wherein R and R¹ are hydrogen; R² is
 chlorine or methoxy; R³ is hydrogen, 3-chlorine, 4-methoxy or 3-dimethylamino
 and R⁴ is 4-chlorine, 4-CH₃SO₂- or 4-CF₃SO₂; and R⁵ is hydrogen and their
 salts.

10 6. The process of Claim 2 wherein R² is chlorine and their salts.

7. The process of Claim 1 wherein R is methyl, R¹ is methyl,
 R² is chlorine, R³ is hydrogen, R⁴ is hydrogen, and R⁵ is 6-chlorine and
 its salts.

8. The process of Claim 1 wherein R is hydrogen, R¹ is hydro-
15 gen, R² is chlorine, R³ is hydrogen, R⁴ is hydrogen, R⁵ is 6-chlorine
and its salts.

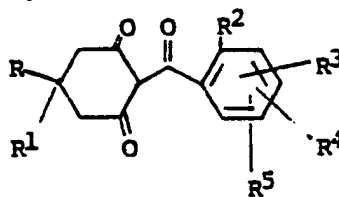
9. The process of Claim 1 wherein R is hydrogen, R¹ is hydro-
gen, R² is chlorine, R³ is hydrogen, R⁴ is 4-chlorine and R⁵ is hydrogen
and its salts.

10. The process of Claim 1 wherein R is hydrogen, R¹ is hydro-
20 gen, R² is chlorine, R³ is 3-chlorine and R⁴ is hydrogen and R⁵ is
6-chlorine and its salts.

11. The process of Claim 1 wherein R is hydrogen, R¹ is hydro-
gen, R² is chlorine, R³ is hydrogen, R⁴ is hydrogen and R⁵ is 5-trifluoro-
25 methyl and its salts.

12. The process of Claim 1 wherein R is hydrogen, R¹ is hydro-
gen, R² is chlorine, R³ is 3-chlorine, R⁴ is 4-chlorine and R⁵ is hydrogen
and its salts.

13. The process of Claim 1 wherein R is hydrogen, R¹ is hydrogen, R² is chlorine, R³ is 3-chlorine, R⁴ is 4-methoxy and R⁵ is hydrogen and its salts.
14. The process of Claim 1 wherein R is hydrogen, R¹ is hydrogen, R² is chlorine, R³ is hydrogen, R⁴ is 4-bromine and R⁵ is hydrogen and its salts.
15. The process of Claim 1 wherein R is hydrogen, R¹ is hydrogen, R² is methoxy, R³ is 3-methoxy, R⁴ is hydrogen and R⁵ is hydrogen and its salts.
16. The process of Claim 1 wherein R is isopropyl, R¹ is hydrogen, R² is chlorine, R³ is hydrogen, R⁴ is 4-chlorine and R⁵ is hydrogen and its salts.
17. The process of Claim 1 wherein R is isopropyl, R¹ is hydrogen, R² is chlorine, R³ is 3-CH₃, R⁴ is 4-CH₃SO₂ and R⁵ is hydrogen and its salts.
18. The process of Claim 1 wherein R is hydrogen, R¹ is hydrogen, R² is chlorine, R³ is hydrogen, R⁴ is 4-CH₃SO₂ and R⁵ is hydrogen and its salts.
19. The process of claim 12 comprising preparing the sodium, isopropylamine, triethylamine and potassium salts of the compound of Claim 12.
20. The method of controlling undesirable vegetation comprising applying to the area where control is desired, an herbicidally effective amount of a compound having the formula

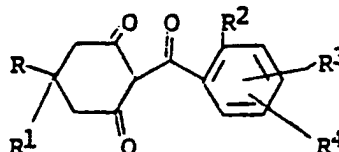


wherein

R and R¹ are hydrogen, C₁-C₄ alkyl, R^aOC(O)-, where R^a is C₁-C₄ alkyl;

R² is chlorine, bromine, iodine or C₁-C₄ alkoxy; and

R³, R⁴ and R⁵ independently are hydrogen or an aliphatic group with
5 the proviso that compounds having the structural formula



wherein

R and R¹ are hydrogen or C₁-C₄ alkyl;

R² is chlorine, bromine, or iodine;

R³ is hydrogen, iodine or chlorine; and

10 R⁴ is hydrogen, halogen, C₁-C₄ alkyl, C₁-C₄ alkoxy, nitro, or trifluoromethyl are excluded.

21. The method of Claim 20 wherein R and R¹ are hydrogen or C₁-C₄ alkyl; R² is chlorine, bromine, iodine or C₁-C₄ alkoxy; R³, R⁴ and R⁵ independently are hydrogen, halogen, C₁-C₄ alkyl, C₁-C₄ alkoxy, OCF₃; cyano, nitro, C₁-C₄ haloalkyl, R^bSO_n wherein R^b is C₁-C₄ alkyl; C₁-C₄ haloalkyl, phenyl, benzyl, -NR^dR^e wherein R^d and R^e independently are hydrogen and C₁-C₄ alkyl; and n is the integer 0, 1 or 2; R^cC(O)NH- wherein R^c is C₁-C₄ alkyl; R^fC(O)- wherein R^f is hydrogen, C₁-C₄ alkyl, C₂-C₄ haloalkyl, C₁-C₄ alkoxy; or -NR^gR^h wherein R^g and R^h independently are hydrogen or
15 20 C₁-C₄ alkyl and their salts.

22. The method of Claim 20 wherein R and R¹ are hydrogen or methyl; R² is chlorine or methoxy; R³ is hydrogen, chlorine or methoxy; R⁴ is hydrogen, chlorine, nitro, SO₂CH₃, SO₂N(CH₃)₂ or CF₃; and R⁵ is hydrogen and their salts.

23. The method of Claim 22 wherein R³ is substituted at the 3-position, R⁴ is substituted at the 4-position and R⁵ is substituted at the 5- or 6-position and their salts.

24. The method of Claim 22 wherein R and R¹ are hydrogen; R² is chlorine or methoxy; R³ is hydrogen, 3-chlorine, 3-methoxy or

3-dimethylamino; R^4 is 4-chlorine, 4- CH_2SO_2 , or 4- CF_3SO_2 ; and R^5 is hydrogen and their salts.

25. The method of Claim 24 wherein R^2 is chlorine and their salts.

5 26. The method of Claim 20 wherein R is methyl, R^1 is methyl, R^2 is chlorine, R^3 is hydrogen, R^4 is hydrogen, and R^5 is 6-chlorine and its salts.

27. The method of Claim 20 wherein R is hydrogen, R^1 is hydrogen, R^2 is chlorine, R^3 is hydrogen, R^4 is hydrogen, R^5 is 6-chlorine
10 and its salts.

28. The method of Claim 20 wherein R is hydrogen, R^1 is hydrogen, R^2 is chlorine, R^3 is hydrogen, R^4 is 4-chlorine and R^5 is hydrogen and its salts.

29. The method of Claim 20 wherein R is hydrogen, R^1 is hydrogen, R^2 is chlorine, R^3 is 3-chlorine and R^4 is hydrogen and R^5 is
15 6-chlorine and its salts.

30. The method of Claim 20 wherein R is hydrogen, R^1 is hydrogen, R^2 is chlorine, R^3 is hydrogen, R^4 is hydrogen and R^5 is 5-trifluoromethyl and its salts.

20 31. The method of Claim 20 wherein R is hydrogen, R^1 is hydrogen, R^2 is chlorine, R^3 is 3-chlorine, R^4 is 4-chlorine and R^5 is hydrogen and its salts.

32. The method of Claim 20 wherein R is hydrogen, R^1 is hydrogen, R^2 is chlorine, R^3 is 3-chlorine, R^4 is 4-methoxy and R^5 is hydrogen
25 and its salts.

33. The method of Claim 20 wherein R is hydrogen, R^1 is hydrogen, R^2 is chlorine, R^3 is hydrogen, R^4 is 4-bromine and R^5 is hydrogen and its salts.

34. The method of Claim 20 wherein R is hydrogen, R¹ is hydrogen, R² is methoxy, R³ is 3-methoxy, R⁴ is hydrogen and R⁵ is hydrogen and its salts.

35. The method of Claim 20 wherein R is isopropyl, R¹ is hydrogen, R² is chlorine, R³ is hydrogen, R⁴ is 4-chlorine and R⁵ is hydrogen and its salts.

36. The method of Claim 20 wherein R is hydrogen, R¹ is hydrogen, R² is chlorine, R³ is 3-CH₃O, R⁴ is 4-CH₃SO₂ chlorine and R⁵ is hydrogen and its salts.

10 37. The method of Claim 20 wherein R is hydrogen, R¹ is hydrogen, R² is chlorine, R³ is hydrogen, R⁴ is 4-CH₃SO₂ and R⁵ is hydrogen and its salts.

38. The sodium, isopropylamine, triethylamine and potassium salts of the method of Claim 31.

0137963



European Patent
Office

EUROPEAN SEARCH REPORT

Application number

| DOCUMENTS CONSIDERED TO BE RELEVANT | | | EP 84109807.2 | | | | | | | | | | |
|--|---|--|--|---------------------------------------|--|--------|-------|--------|-------|--------|-------|--------|--------|
| Category | Citation of document with indication, where appropriate, of relevant passages | Relevant to claim | CLASSIFICATION OF THE APPLICATION (Int. Cl.4) | | | | | | | | | | |
| X | EP - A1 - 0 017 195 (EISAI CO., LTD.) * Claims 1,9 * | 1 | C 07 C 49/813 C 07 C 49/84 C 07 C 62/38 C 07 C 79/36 | | | | | | | | | | |
| P,X | EP - A2 - 0 090 262 (STAUFFER CHEMICAL COMPANY) * Claims 1-12 * | 1-4,6-14,16,20-33,35 | C 07 C 147/06 C 07 C 149/273 C 07 D 317/62 A 01 N 35/06 | | | | | | | | | | |
| A | US - A - 4 283 348 (THOMAS N. WHEELER) * Abstract * | 1,20 | | | | | | | | | | | |
| A | US - A - 4 227 919 (REED A GRAY et al.) * Abstract * | 1,20 | | | | | | | | | | | |
| A | US - A - 4 256 658 (THOMAS N. WHEELER) * Abstract * | 1,20 | <table border="1"> <thead> <tr> <th colspan="2">TECHNICAL FIELDS SEARCHED (Int. Cl.4)</th> </tr> </thead> <tbody> <tr> <td>C 07 C</td> <td>49/00</td> </tr> <tr> <td>C 07 C</td> <td>62/00</td> </tr> <tr> <td>C 07 C</td> <td>79/00</td> </tr> <tr> <td>C 07 C</td> <td>147/00</td> </tr> </tbody> </table> | TECHNICAL FIELDS SEARCHED (Int. Cl.4) | | C 07 C | 49/00 | C 07 C | 62/00 | C 07 C | 79/00 | C 07 C | 147/00 |
| TECHNICAL FIELDS SEARCHED (Int. Cl.4) | | | | | | | | | | | | | |
| C 07 C | 49/00 | | | | | | | | | | | | |
| C 07 C | 62/00 | | | | | | | | | | | | |
| C 07 C | 79/00 | | | | | | | | | | | | |
| C 07 C | 147/00 | | | | | | | | | | | | |
| The present search report has been drawn up for all claims | | | | | | | | | | | | | |
| Place of search VIENNA | | Date of completion of the search 27-11-1984 | Examiner REIF | | | | | | | | | | |
| <p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document</p> | | | | | | | | | | | | | |